# Reporting Electrode Potentials in Ionic Liquids

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Ionic liquids (IL's) are being studied for several electrochemical applications, e.g. as electrolytes with broad electrochemical windows. It is important in electrochemistry to locate the exact position of the potentials at which the processes occur. As ionic liquids are used as 'tuneable' solvents a suitable reference system should even be able to allow comparison of the position of the potential of a process in different ionic liquids.
Aqueous standard reference electrodes, such as the Ag/AgCl in saturated KCl, are to be avoided because of the liquid junction potential (LJP) existing at the separator between both solutions and the risk in some applications of contaminating the process with water. Often pseudo-references like a platinum or silver wire are used. Although a junction is clearly not present here, a serious drawback is that the potential they are referring to is related to conversion reactions of the IL and therefore their use as reference electrode is doubtful. Reference electrodes in non-aqueous molecular solvents[1] are well-described as well and avoid some of the problems encountered with aqueous reference electrodes, but especially the LJP is still troublesome. Another option is to use reference electrodes based on the same IL the process uses. Still they don't supply an accurate way to compare electrode potentials between ionic liquids and other electrolytes. Moreover, the high viscosity of many IL's leads to a high resistance at the junction and thus result in difficult and unreliable measurements.
A system for referencing formal potentials commonly used in molecular non-aqueous solvents, is the addition to the solution of small quantities of internal references such as ferrocene or bis-(biphenyl)chromium recommended by IUPAC[2]. Even though ferrocene is the most popular amongst the internal references and often used in ionic liquids, there are several issues concerning its stability[3-5]. Cobaltocene is suggested to replace ferrocene[6] but comparable data in molecular solvents lack.
Although referencing by means of internal reference compounds seems to be very suitable for comparison in different IL's, while avoiding errors because of LJP, few research has been conducted on this subject. Because of the wide variety of IL's it can be expected that not all compounds used as internal reference are suitable for every IL, e.g. because of limited solubility. Therefore, it seems useful to provide a 'set' of compounds that allow comparison even in quite different IL's. In this work several compounds are studied for their potential to be used as internal references. Besides the three commonly used references mentioned earlier, other redox couples based on strong aqueous complexes of iron, cobalt, ruthenium, iridium and palladium are tested on the criteria for internal references[2].

References
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